

**REMARKS**

The Examiner should withdraw the rejection of claims 1 – 9 under 35 U.S.C §103(a) over *Mohrschladt et al.* (US 6,316,588) or *Mohrschladt et al.* (US 6,288,207), made in the non-final Office action mailed August 21, 2007.

The Examiner has ceased arguing that the examples presented in the specification do not compare the invention to the closest prior art. Instead, the Examiner has assumed “that the closest prior art exemplified by the references … [uses a] catalyst with BET surface area of 50 m<sup>2</sup>/g....”<sup>1</sup> Applicants note that this assumption is in line with the facts. However, the Examiner continued to incorrectly correlate the BET surface area of catalyst particles with the “size” of catalyst particles by stating that:

it is known in the art of catalysts that smaller size [*sic*] catalyst particles (particles having higher BET area) gets [*sic*] trapped in the final polymeric product more easily, thus the amount of smaller size [*sic*] catalyst is expected to be higher in the final product as compared to the catalyst of the larger particle size.<sup>2</sup>

The Examiner has provided no support for this assertion. Yet, based on this assertion the Examiner concludes that the results on pages 14 – 15 of the specification are not unexpected.<sup>3</sup> To refute the Examiner’s erroneous assertion, Applicants are happy to provide the Examiner with the enclosed copy of “Heterogeneous Catalysis for the Synthetic Chemist, R.L. Augustine, Marcel Dekker, Inc., New York – Basel – Hong Kong, 1996, Chapter 9, Catalyst Support, pages 155 and 156.” This reference explains that:

There are a number of physical characteristics of the support that are important for the proper performance of the supported catalyst. These are hardness, density, pore volumen, pore size, pore distribution, particle size and particle shape. ... Generally one considers that the maximum surface area for the support or catalyst is the best possible arrangement but this is not always true. First it

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<sup>1</sup> Page 2, lines 24 – 25 of the present Office action.

<sup>2</sup> Page 3, lines 6 – 10 of the present Office action.

<sup>3</sup> Page 3, lines 2 – 3 of the present Office action.

must be recognized that the surface area is not only associated with the external surface of the particle but also with the surface of all the pores within the particles. A particle having small diameter pores will have a higher surface area than one having larger diameter pores with both having the same total pore volume.

In light of this clear explanation, Applicants hope that the Examiner will no longer maintain the erroneous position that smaller sized catalyst particles are particles that have higher BET surface area. This erroneous position seems to have hindered the Examiner's understanding of the claimed invention, as well as the showing of unexpected results achieved by the claimed invention.

As explained in the previous reply, Applicants have stated under oath in the present specification that:

Surprisingly, it has been found that the reduction in catalyst activity claimed in the prior art for the BET surface area of the catalyst of the present invention does not occur, the catalyst activity in the process of the invention in fact being just as high as in the process described in WO 99,38906, WO 99/38908, and WO 01/09224.

Applicants have also demonstrated that a surprising reduction in the titanium dioxide content of polymer is achieved by the process according to the present invention. This unexpected result is evidenced by comparison of example 1 (a catalyst according to the present invention, having a BET surface area of 30 m<sup>2</sup>/g) with comparative example 1 (a catalyst equivalent to the catalyst of US 6,316,588 having the lowest exemplified BET surface area, i.e. a BET surface area of 50 m<sup>2</sup>/g).<sup>4</sup> As shown in Table 1, use of the inventive catalyst results in an unexpectedly decreased titanium dioxide content of polymer after 24 hours, 48 hours, 96 hours, 144 hours, and 240 hours of operation.

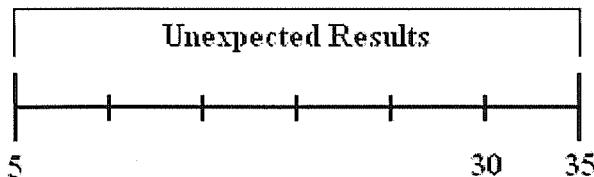
The mere fact that these unexpected results are not discussed in a paragraph beginning with the word "surprisingly" does not render them expected. Thus, the Examiner erred by focusing exclusively on "the paragraph bridging pages 13 and 14 of

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<sup>4</sup> The MPEP makes clear that "[a]n applicant does not have to test all the compounds taught by each reference...."<sup>4</sup> Thus, the comparative tests reported on pages 14 – 15 of the present specification are sufficient to permit a conclusion respecting the relative effectiveness of applicant's claimed compounds and the compounds of the cited references.

the instant application[,]”<sup>5</sup> and by arguing that “[w]hat was considered unexpected ... was ... that the catalytic activity of the catalyst with smaller BET ... does not decrease as compared to the catalytic activity of the larger BET area catalysts.”<sup>6</sup>

Finally, the Examiner’s comments regarding whether the showing of unexpected results are commensurate in scope with the claimed invention are in error. The Examiner argues that “the original claims and the specification referred to the upper limit 35 [m<sup>2</sup>/g] as within the scope of the ‘present invention’ ... and not the presently claimed [upper limit of] 30 [m<sup>2</sup>/g].”<sup>7</sup> MPEP §716.02(d) explains that “the ‘objective evidence of nonobviousness must be commensurate in scope with the claims which the evidence is offered to support.’ In other words, the showing of unexpected results must be reviewed to see if the results occur over the entire claimed range (emphasis added).” The following illustration might be helpful.



If unexpected results were originally shown over the entire range of from 5 to 35 m<sup>2</sup>/g, then the unexpected results were also shown over the entire range of from 5 to 30 m<sup>2</sup>/g.

The rejection is in error and should be withdrawn. Favorable action is respectfully solicited.

<sup>5</sup> Page 3, lines 15 – 16 of the present Office action.

<sup>6</sup> Page 3, lines 11 – 14 of the present Office action.

<sup>7</sup> Page 3, lines 21 through page 4, line 1 of the present Office action.

In Conclusion:

The present application is in condition for allowance. Again, applicants are thankful for the Examiner's diligent efforts to advance this application to allowance, and request favorable action in this matter. In order to facilitate the resolution of any issues or questions presented by this paper, the Examiner is welcome to contact the undersigned by phone to further the discussion.

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Enclosure (1): Heterogeneous Catalysis for the Synthetic Chemist, R.L. Augustine, Marcel Dekker, Inc., New York – Basel – Hong Kong, 1996, Chapter 9, Catalyst Support, pages 155 and 156.

# HETEROGENEOUS CATALYSIS for the SYNTHETIC CHEMIST

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of the development of hydrogenation technology, they were too specific and not the general procedures that were implied. The current book presents a more detailed discussion of the effects that the various reaction parameters can have on reaction selectivity so the reader can apply these concepts to the development of optimal reaction conditions for the preparation of specific compounds. The generally useful procedures are still given, but not emphasized as before.

Another departure from the previous text is the inclusion of chapters on other heterogeneously catalyzed reactions such as oxidations, solid acid and base catalyzed reactions and the like, as well as a more thorough coverage of the catalysts themselves. Not only are metal catalysts discussed but also the simple and complex oxides, the zeolites and clays, both as catalysts in their own right as well as being potential supports for the catalytically active metals. The factors involved in the preparation of the catalysts are also discussed in sufficient detail that the reader will understand the problems associated with catalysts having specific properties needed for obtaining optimal selectivity in a given reaction.

Grateful appreciation is given to my colleagues and students who have read portions of the manuscript and provided helpful suggestions for its improvement, especially Dr. Setrak, K. Tanieyan, Dr. Leslie Scott, Szivos, Dr. Lisa K. Doyle, Dr. Sanjay V. Malhotra, Sr. Leo S. Posner, Dr. Steven Roberto and Dr. John R. Sowa. Special thanks and appreciation must go to my wife, Marilyn, for her patience, understanding and the encouragement to stay with this project to its completion.

*Robert L. Augustine*

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function of the particular catalyst, the temperature and the time the catalyst is exposed to the heat. For most catalytically active metal powders sintering can be observed at temperatures as low as 100°C but oxide catalysts can generally be used at higher temperatures without a significant loss of active surface area. If the catalytically active particulates can be kept separate from each other thermal agglomeration can be eliminated or, at least, minimized. The most effective way of accomplishing this is to attach the catalyst species to the surface of a thermostable support material as shown in Fig. 9.1c. For comparison, a powdered platinum black catalyst can sinter at temperatures as low as 100°C but a supported catalyst, such as Pt/Al<sub>2</sub>O<sub>3</sub>, does not usually sinter at temperatures under 450–500°C.

The environment of the dispersed catalyst particulates in these supported catalysts is influenced by a number of factors, primarily the relative amount of catalytically active material present, the nature of the support and the strength of the interaction between the support and the catalyst particles. Metal catalysts having a low metal load are usually composed of very small crystallites widely scattered over the surface of the support (Fig. 9.1c). Such crystallites generally have a high dispersion so the metal is efficiently used. As the metal load increases the crystallites are closer together and, also, frequently larger in size (Fig. 9.1b). The further apart the crystallites, the more resistant they are to thermal sintering. Obviously, if the catalyst crystallites are in contact with each other, thermal coalescence can be expected to take place with a resulting loss of active surface area. However, as shown in Fig. 9.1b, the presence of the support can limit the size of the sintered particles.

A second sintering mechanism, which applies primarily to metals, involves the interaction of the metal with some species in the reaction medium to form a surface intermediate that is sufficiently volatile that it can migrate from one particle to another. Since smaller metal particles have a higher percentage of their component atoms on the surface than larger ones, the formation of a volatile surface species will be favored on the smaller crystallites and the result will be the growth of the larger particulates and the loss of the smaller ones. Halide ions frequently promote sintering by this mechanism so every effort should be made to remove them from the catalyst when metal halides are used in the preparation procedure. A strongly reducing atmosphere can also facilitate metal sintering at high temperatures<sup>2</sup> but this can be minimized by running the reduction at a lower temperature, if possible.

The objective in the preparation of supported catalysts is to have the catalytically active crystallites separated. When this is the case the only way sintering can occur is if the catalyst particulates migrate across the support surface or if there is a vapor phase sintering promoter present in the reaction medium. The lower the catalyst load and the higher the support surface area, the less likely that sintering will take place. The migration ability of the catalytically active species depends primarily on the strength with which it is bonded to the support. If there is a weak interaction the catalyst particles can move across the support

surface and sintering may occur at temperatures only slightly higher than those needed to coalesce the unsupported material. On the other hand, if the interaction is very strong it approaches chemical compound formation on the support surface with a possible loss in catalytic activity. With most supported catalysts the support interaction is, ideally, somewhere between these extremes. A more complete discussion of the catalyst support interaction is found at the end of this chapter.

While the low metal load, highly dispersed catalysts provide a maximum surface area per unit weight of metal, those catalysts having larger catalyst particulates spread over most of the support surface provide a maximum metal surface area per volume of catalyst.<sup>1</sup> Generally the more expensive precious metal catalysts have low metal loads and are highly dispersed while catalysts containing the less expensive base metals have higher metal loadings, usually 20–40% or higher. The relationship between the catalyst load and crystallite size or catalyst dispersion is dependent on a number of factors, of which one of the more important is the surface area of the support.

The support can also be used to absorb small quantities of materials that are toxic to the catalyst and, thus, prevent them from interacting with the catalytically active surface. Activated carbon supports are particularly effective in this regard.

There are a number of physical characteristics of the support that are important for the proper performance of the supported catalyst.<sup>3</sup> These are hardness, density, pore volume, pore size, pore distribution, particle size and particle shape. The surface area is directly related to pore size, distribution and volume. Support particles must be sufficiently hard to withstand the abrasion associated with the type of process in which they are to be used so they will not be broken down into smaller particles and thus change the operating conditions of the system. In flow processes using a fixed bed reactor the catalyst particles must be able to withstand the pressure and vibration induced by the flow of the reaction medium. The breakdown of the catalyst into finer particles can have a significant impact on the flow characteristics of the reactor. Reactions run in a fixed bed reactor usually require larger supported catalyst pellets to keep the pressure drop over the catalyst bed at an acceptable level. Reactions run in a batch mode using a stirred autoclave generally use catalysts composed of small support particles so the catalyst can be efficiently suspended in the reaction medium by the action of the stirrer. The density of the catalyst must be such as to provide the optimum suspension in the reaction medium. In a stirred reactor, particle breakdown can change the suspension characteristics of the catalyst and also increase the difficulty of subsequent catalyst separation from the reaction medium.

Generally, one considers that the maximum surface area for the support or catalyst is the best possible arrangement but this is not always true. First it must be recognized that the surface area is not only associated with the external surface of the particle but also with the surface of all the pores within the particles. A particle having small diameter pores will have a higher surface area than one

having larger diameter pores with both having the same total pore volume. For vapor phase reactions involving small molecules, catalyst particles having a large number of smaller pores and higher surface areas are preferred since the multitude of pores provides access of the smaller reactant molecules to the catalytically active sites present throughout the catalyst particles. Reactions of synthetic interest, however, generally involve larger molecules and are usually run in a liquid medium. For such reactions, catalysis having the smaller pores are inefficient since the diffusion restraints would severely hinder the reaction. Catalysts for these reactions, then, should have larger pores with the catalytically active sites located near the surface of the support particles so diffusion of the reactants to the active sites will not be a significant factor in the reaction.

Since all of these characteristics are related it is necessary to balance one against the other to optimize the performance of the catalyst. Highly porous catalysts will have a low density and be relatively easy to break down into smaller particles. As the hardness and abrasion resistance of the particle increases, though, the porous nature decreases so some balance must be sought to optimize the catalyst for a specific application.<sup>3</sup>

It is obvious from this discussion that control of pore size and distribution is important in developing the optimum catalyst for a specific process. The most common perception of the pores in a catalyst particle is that they are essentially holes of various diameters drilled into the particle at various angles or, perhaps, they resemble various sized tunnels randomly oriented throughout the particle. While such representations may be helpful in discussing the effects of pore diffusion and similar catalytic factors, it does not provide any basis for the development of methods that can produce supports or supported catalysts having specific pore characteristics.

For this purpose it is best to understand the development of the porous structure of a given solid particle. All solids are built up from individual units that can be molecules, a unit crystal or, even, a small densely packed arrangement of molecules or unit crystals. This basic building block is denoted as A in Fig. 9.2. The coalescence of several of these units gives a larger system, B, with small interces between the basic units. These are designated as Type I pores. Coalescence of several B units forms a larger system, C, in which larger, Type II, pores are also present. Further agglomeration of C units gives D in which the Type III pores are even larger.<sup>3</sup>

Pore size and distribution can be regulated by controlling the size of the initial building block, A, and the size of the final particle, such as D in Fig. 9.2. The larger the A particle is, the larger the Type I pores are. If A is large enough and the final particle size is held to B, then a narrow pore size distribution will result. The problem is to have a sufficiently large initial species, A, so that B will be reasonably large to be useful as a support. This is sometimes accomplished using a colloidal particle, such as silica gel, as the initial building block. Such colloidal species can have small interces as well but they are of atomic scale and relatively unimportant in catalysis. A more common system is represented by C in which there is a bimodal distribution of pores, that is, small Type I and larger Type II.

Not only does the size of the basic building block effect the final pore sizes but the shape of the particle is also important. Large, irregularly shaped particles will pack loosely on agglomeration with the production of large pores. If small particles are also present they may pack into the voids thus reducing the porosity of the material considerably.<sup>4</sup> If the basic building block, A, or any of the other larger systems do not coalesce in a uniform, close packed manner, the pore size will be dependent on the extent of linear "polymerization" and branching as depicted in Fig. 9.3.<sup>5</sup>

Another method of controlling pore size distribution is to incorporate an additive into the system during the preparation of the support and then to remove it selectively after the support particles have been formed. Common materials used for this purpose are pieces of cellulose, cotton, or other carbonaceous material that can be removed by ignition to leave behind voids corresponding to the shape of the added material.<sup>4</sup>

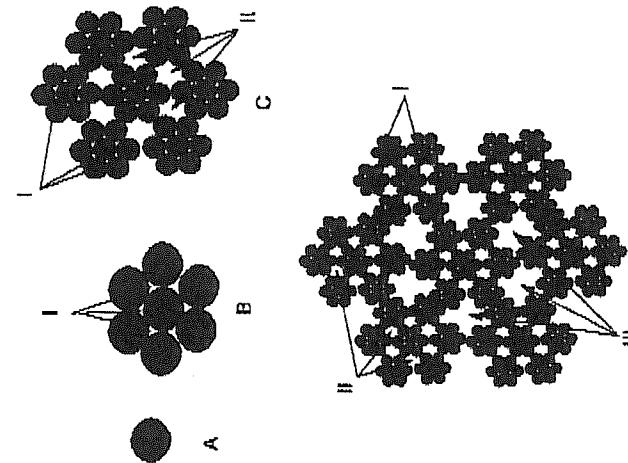


Fig. 9.2. Pore development in the agglomeration of the basic unit, A, into progressively larger particles.